Project Summary - Grant # 47589-CH
(Reporting Period: May 2005 – April 2008)

Fundamental Investigations of Durability at a Polymer Electrolyte-Electrode Interface

PI Name: Professor Sanjeev Mukerjee
Department: Chemistry and Chemical Biology
Institution, City, State, Zip: Northeastern University, Boston, MA 02115

Objective

The overall objectives of this proposed effort was to further our fundamental understanding of degradation pathways at a polymer electrolyte-electrode interface. Towards this goal the key thrust areas proposed in this project were:

(1) Understanding the role of peroxide lead free radical attack on the polymer electrolyte at the interface with both anode and cathode electrodes using a specially designed PEM cell enabling accelerated degradation conditions simulating practical H_2/Air PEM operation. In this effort the correlation was made with peroxide yield measured directly using RRDE methods with concomitant degradation of the membrane and ionomer.

(2) Understanding the effect of Ru stability in a variety of PtRu electrocatalysts under various DMFC operating conditions and the effect of its migration and deposition at the cathode. A combination of fuel cell studies and rotating disk electrode method are used to quantify the losses at both anode and cathode electrodes, these are correlated with the nature of the PtRu/C bulk and surface properties.

(3) Understanding the effect of alloying on the stability of cathode electrocatalysts under various fuel cell operating conditions, especially at open circuit conditions.

Approach:

(1) Tailored synthesis of electrocatalysts for probing specific aspects of electrocatalyst degradation. These include micellar methods for preparation of monodispersed crystallites with both homogeneous and core shell structures.
(2) Application of in situ advanced synchrotron based x-ray absorption methods for investigating changes to the short range atomic order and site specific adsorption modes on transition metal surfaces. Specific aspects of corrosion, dissolution surface segregation were probed as a function of various PEM fuel cell operating conditions.
(3) Specifically designed accelerated durability protocols were established using a unique segmented cell set up. This allowed for probing polymer electrolyte stability at the interface with both anode and cathode electrodes. Correlation with other standard techniques such as RRDE, step scan IR studies etc. were used to complete our understanding of the specific degradation process.

Relevance to Army

Understanding durability from the perspective of materials preparation, morphology, bulk and surface characteristic are designed to provide the Army with benchmarks for various devices under consideration for future combat missions and soldier power. Such understanding is expected to show the way towards more active and stable choice of materials and provide the window of operation to ensure long term reliability.

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Accomplishments for Reporting Period

- Correlation with catalyst bulk and surface characteristics with corresponding peroxide yield.
- Validation of accelerated test methodology for correlation of peroxide yields and interfacial stability of the membrane.
- Understanding the effect of Ru migration at the cathode electrode in a DMFCs and the evolution of materials consideration for a stable PtRu anode.
- Fundamental understanding of Pt surface poisoning from halide ions.

Collaborations and Technology Transfer

- Establishment of collaborative efforts with catalyst vendors, these include BASF-ETEK, and Cabot-Superior Micropowders.
- Establishment of joint efforts for understanding interfacial stability of perfluorinated membranes and ionomers with W. L. Gore, BASF and Advent N.A.
- Understanding durability for specific device considerations with Encite llc.
- Development of Ultra-stable PtRu Electrocatalysts.

These are to translate the results of this research to the industry and incorporation into actual devices.

Resulting Journal Publications During Reporting Period (May 2005 onwards)

(1) 'Investigation of Durability Issues of Selected Nonfluorinated Proton Exchange Membranes for Fuel Cell Applications', L. Zhang and S. Mukerjee, *J. Electrochem. Soc.,* **153**, A 1062

(2) 'CO Coverage/Oxidation Correlated with PtRu Electrocatalyst Particle Morphology in 0.3 M Methanol by in situ XAS', F. Scott, D. Ramaker and S. Mukerjee, *J. Electrochem. Soc.*, **154**, A 396 (2007).

(3) Specific vs. Non Specific Absorption of Anions on Pt and Pt based Alloys, M. Teliska, S. Mukerjee and D. Ramaker, *J. Phys. Chem. C,* **111,** 9267 (2007)

(4) 'The Impact of Ru Contamination of a Pt/C Electrocatalyst on Its Oxygen Reduction Activity', L. Gancs, B. Hult, N. Hakim and S. Mukerjee, *Electrochem. Sol. St. Lett.,* **10**, B150 (2007)

(5) 'Degradation Mechanism Study of Perfluorinated Proton Exchange Membrane under Fuel Cell Operating Conditions' N. Ramaswamy, N. Hakim and S. Mukerjee, *Electrochim. Acta*, **53**, 3279 (2008).

(6) 'Enhanced Activity and Intefacial Stability Study of Ultra-Low Pt based Electrocatalysts Prepared by Ion Beam Assisted Deposition', N. Ramaswamy, T. M. Arruda, W. Wen, N. Hakim, M. Saha, A. Gulla and S. Mukerjee, Electrochim Acta, *In Press*

(7) 'Impact of Ru Dissolution and Migration in a DMFCs Environment' S. Shyam, T. Arruda, D. Ramaker and S. Mukerjee, *J. Phys. Chem.,* (Submitted May 2009)

Graduate Students Involved

- Lei Zhang (graduate student). Received Ph.D degree in May 2006
- Nagappan Ramaswamy (graduate student)
- Dr. Lajos Gancs (Postdoctoral Research Associate) [Part time support]

Awards, Honors and Appointments

- Awarded the Klein Memorial Award at Northeastern University, April 2007

Understanding the Nature of Interfacial Degradation of Polymer Electrolytes due to Peroxide lead Free Radical Attack

Student: Lei Zhang (Graduated May 2006) and Nagappan Ramaswamy (2nd year graduate student)

Novel accelerated technique was used to investigate and correlate the peroxide generation at an electrode/electrolyte interface from the perspective of radical initiated perfluorinated membrane degradation as a function of choice of electrocatalyst, catalyst loading on carbon support, operating overpotential, temperature, and presence of alloying element on the surface against Pt rich outer layer. Membrane degradation process was studied in half cell configurations using a novel segmented cell design (see figure 1 in inset) so that the two formerly proposed PEM degradation mechanisms could be evaluated individually without interference. Details of this methodology are published earlier.[1] Peroxide generation observed on the ring electrode of a RRDE for various electrocatalysts used in this study showed a one-on-one relation with the level of degradation of perfluorinated membrane via local Fenton type reactions at the cathode-membrane interface of an operating fuel cell due to the simultaneous 2e$^-$ pathway of ORR along with the more predominant 4 e$^-$ reduction to water.. This is exemplified by tables 1 and 2 wherein the peroxide yields are shown along with the corresponding changes in the proton conductivity and ion exchange capacity after subjecting the cell to accelerated cathode side condition shown in figure 2 (Lhs).

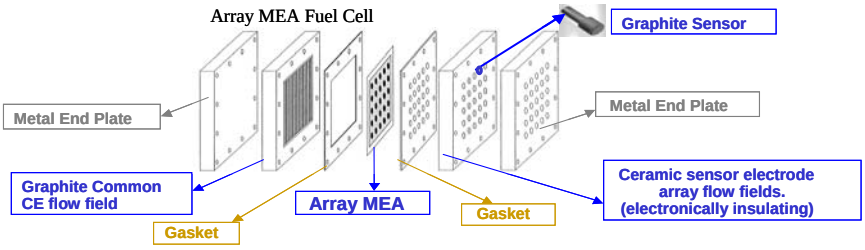

Fig 1: Experimental Setup for Durability Study

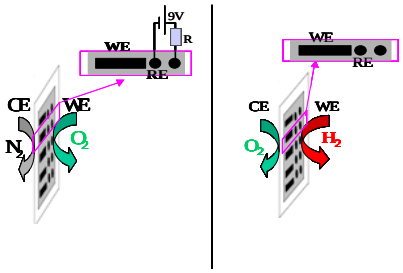

Figure 2. Schematic for evaluating peroxide initiated chemical attack at cathode and anode electrodes respectively in a segmented PEM cell.

Catalyst	%H_2O_2 @0.7V	%H_2O_2 @0.6V	%H_2O_2 @0.4V
30% Pt/C	0.111	0.257	2.330
60% Pt/C	0.394	0.753	2.408
Pt_2Co/C	0.342	0.652	3.523
Pt_3Co/C	0.160	0.260	0.510

Table 1: Peroxide yields (mole fraction) measured using a RRDE technique with a rotation rate of 900 rpm and various disk potentials of 0.7V, 0.6V, 0.4V Vs RHE in conjunction with a gold ring electrode polarized at 1.3V in 1M $HClO_4$ at room temperature.

Catalysts	WE @ 0.4 V		WE @ 0.6 V	
	$\frac{\sigma_{after}-\sigma_{before}}{\sigma_{before}}$ (%)	$\frac{\eta_{after}-\eta_{before}}{\eta_{before}}$ (%)	$\frac{\sigma_{after}-\sigma_{before}}{\sigma_{before}}$ (%)	$\frac{\eta_{after}-\eta_{before}}{\eta_{before}}$ (%)
30% Pt/C	34	26	27	19
60% Pt/C	57	48	49	43
30% Pt_2Co/C	50	40	44	34
30% Pt_3Co/C	27	22	16	9

Table 2. Effect of cathode side durability tests with O_2/N_2, 40°C, 1 atm, for a duration of 24 hours using 30% Pt/C, 60% Pt/C, 30% Pt_2Co, 30% Pt_3Co at two different working electrode (WE) polarization potentials of 0.4 V and 0.6 V Vs DHE. Listed are the decreases in proton conductivity σ (S cm^{-1}) and ion exchange capacity η (mEq g^{-1}).

Cleavage of the side chain ether linkage (Fig. 3), which intrudes into the hydrophilic ionic cluster, is found to be the key initiator of conductivity and ion exchange capacity loss. Prolonged durability testing leads to breakage of certain sections of fluorocarbon backbone as observed in the stabilization of ion exchange capacity vs. a more linear decline in proton conductivity (Table 2). Normal operating cathode overpotentials of 0.6 and 0.7 V Vs RHE leads to lower membrane degradation relative to higher overpotentials of 0.4 V, this is directly correlated to peroxide yields measured

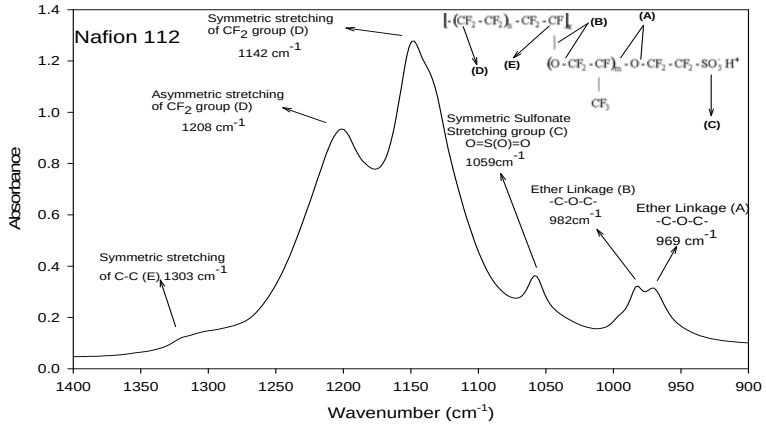

Figure 3: ATR-FTIR Spectrum of Nafion®112 (H-form) indicating absorption bands obtained using ZnSe ATR crystal. [See text for references]

independently in RRDE. Higher the loading of catalyst on carbon support and corresponding larger the particle size results in higher peroxide yield and consequent higher membrane degradation as shown by the comparison between 60% Pt/C and 30% Pt/C used in this study. PtCo/C alloy catalyst with enrichment of surface Co gives lower peroxide current and maintains lower level of membrane degradation as shown by the comparison between Pt_2Co/C and Pt_3Co/C. Temperature effects on membrane degradation was found to be linear with higher ORR activity and consequent higher peroxide generation at the interface. Degradation at the anode side due to oxygen crossover through the membrane was found to be insignificant relative to cathode side degradation within the duration of the experiments performed here. However these tests represent the narrow confines of interaction of absorbed hydrogen on Pt and its interaction with crossover oxygen.

Fundamental Aspects of Ru Dissolution and Migration under DMFC Operating Environment
Student: Thomas Arruda (3rd year graduate student)
Postdoctoral Research Associate: Dr. Lajos Gancs (partial support)

In this work, we *explicitly* present the effect of Ru contamination on the ORR kinetics on Pt/C, in order to provide a link to PEMFC performance degradation. In our simplistic experimental approach, Ru was dissolved from a commercial unsupported PtRu electrocatalyst-based fuel cell electrode (referred as sacrificial electrode) directly into the liquid electrolyte, in which oxygen reduction was performed on a thin film Pt/C working electrode. Ru^{n+} concentration was monitored using ICP-MS, while changes in ORR kinetics were addressed by rotating disk electrode experiments. A detailed study showing the Ru contamination under various fuel cell cathode operating conditions such as cathode overpotential, temperature and choice of electrocatalyst (Pt alloy vs. Pt) are presented in the full version of this report.

The kinetics of oxygen reduction on Pt/C can be explicitly followed up from the measured RDE current values after correcting for the mass transport-related contributions. The mass transport of oxygen at a pure Pt surface can be treated in a straightforward fashion since the surface is uniformly accessible to molecular oxygen at a given electrode potential. When the Pt surface is partially covered by Ru, the ORR activity becomes dependent on surface elemental composition due to the different reaction kinetics on the pure metals. Assuming that all Ru adatoms on Pt are oxidized and thereby inactive towards the adsorption of molecular oxygen at low ORR overpotentials (say at or

above 0.8 V), such a Pt-Ru bimetallic surfaces should perform like a pure Pt, albeit blocked by Ru to various extents[2], unless the reaction mechanism changes (*vide infra*). Finding the electrochemical surface area for oxygen reduction at Pt-Ru electrodes however is a rather complicated task, it requires the exact knowledge of elemental composition and surface structure[2] as well as the adsorption energy of surface oxides at a given electrode potential[3]. Nevertheless, the blocking mechanism exerted by Ru is exactly what is analyzed here. This is attained by the comparison of the kinetic current values, which were calculated using Equation (1)[4]:

$$i_k = \frac{i_L \times i_m}{i_L - i_m} \quad (1)$$

i_k was extracted from data corresponding to the mixed kinetics-mass transport region of the RDE polarization curve. We also mention that the current measured at 0.3 V (i_L) is a pseudo-limiting current since the exposed Ru is partially covered by surface hydroxides at that electrode potential.

In Table 3, kinetic current density (j_k*) values are summarized which were obtained for clean and Ru-contaminated Pt/C electrode in 0.5 M H_2SO_4. j_k* was calculated from i_k using and Equation (1) after normalizing it to the mass of Pt. Oxygen reduction is found to be at least 8-times more sluggish when the total number of dissolved Ru atoms is more than 3000-times higher than the number of surface Pt atoms, although the estimated Ru coverage of the Pt surface is less than 20 %. This is conceived based on a comparison of the amount of Ru present in a known concentration within the volume of the electrolyte and the number of Pt atoms exposed, as determined independently from ICP-MS data and from the H_{UPD} area (from the cyclic voltammogram), respectively.

The Tafel pots in Figure 6 do not evidence any significant changes in the mechanism of oxygen reduction in the low overpotential region (between 0.8 V and 0.9V) upon Ru contamination as observed in H_2SO_4. For Pt/C in clean electrolyte, the Tafel slope was found -122 mV decade^{-1}, which is quite close to those obtained for PtRu (-115 mV decade^{-1}) and upon various Ru-contamination (-113 mV decade^{-1}). This hints that at low ORR overpotential, oxygen reduction seems to proceed on the platinum sites exclusively, without the influence of other electrode reaction. The dramatic drop in ORR kinetics at Pt/C as a result of Ru contamination is readily evident from the Tafel-plots. In terms of overpotential, this can translate to a ca. 160 mV increase as the arrow demonstrates in Figure 6. It is interesting to match the kinetic current values obtained for the Pt/C electrode in Ru-contaminated solutions to those measured for a PtRu electrocatalyst (Johnson & Matthey HiSpec6000) in clean electrolyte. For the PtRu electrocatalyst, we have estimated the initial Pt:Ru surface atomic composition to be 0.67 by copper underpotential deposition and subsequent removal[5], and also we consider here that Ru is in intimate contact with Pt in the PtRu electrocatalyst sample.

Table 3: Maximum possible (ΦRu^{max}) and estimated actual (ΦRu^{est}) Ru coverage levels on Pt/C and the corresponding Pt mass-specific kinetic current density (j_k*) values for ORR

		0.5 M H_2SO_4				1 M TFMSA	
c_{Ru}^{n+} [μmol dm^{-3}]		0	147	169	202	0	23
Θ_{Ru}^{max} [ML Pt]		0	2790	3210	3840	0	500
Θ_{Ru}^{est} [ML Pt]		0	0.12	0.18	0.31	0	0.14
j_k* [A cm^{-2} g^{-1}]	0.90 V	28.59	20.27	3.55	3.42	39.32	23.11
	0.85 V	76.78	51.56	10.15	8.87	120.80	80.77
	0.80 V	179.10	112.98	21.44	21.01	291.30	197.89

Furthermore, one can presume that above 0.85 V the Ru surface atoms are completely oxidized and thus do not reduce oxygen. Correcting for a surface blocking factor of 0.43 due to a inactive higher Ru oxidation state, indeed similar kinetic current values could be calculated in the clean electrolyte for both Pt/C and PtRu at low ORR overpotentials. However, several fold lower kinetic current values were measured for the Pt/C electrode when the Ru^{n+} concentration exceeded 150 μmol dm^{-3} as compared to those obtained for the Pt:Ru electrocatalyst in clean electrolyte. The CV data showing H_{upd} based electrochemically active surface area ascribed to Pt sites, is contrary to the above observations on the basis of Ru atoms present on the surface (Table 1). This is exemplified on the basis of the Cu upd measurements of Ru presence on PtRu electrocatalyst where surface coverage of 43 atom percent is reported. The blocking effect of Pt/C in Ru^{n+} solutions was significantly lower (Table 1) when compared in electrolyte containing different Ru^{n+} concentrations. This apparent discrepancy is explained by taking into account the nature of Ru accumulation on Pt in the atomic level. Namely, Ru is expected to reach higher coverage levels on Pt according to the Volmer-Weber growth mechanism, *viz.* by the formation of three-dimensional clusters with heights of several atomic layers.[6] For such electrode structures, the transport and reduction of oxygen can be limited to the topmost Ru atoms while the underlying Pt sites might be less utilized. In other words, the electrode blocking factor is higher than what can be calculated from the ratio of Ru-covered Pt/C and the clean Pt/C H_{UPD}. (Note that the H_{upd} area does not reflect the transport of dissolved oxygen.) This

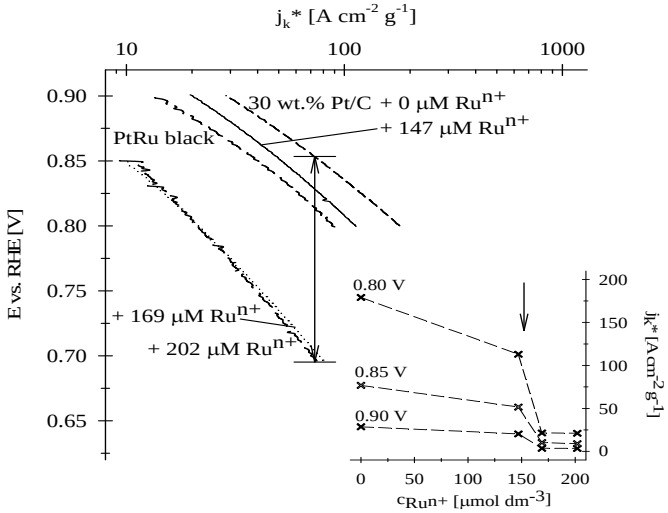

Figure 4. Mass transport-corrected Tafel plots for oxygen reduction on a thin film 30 wt. % Pt/C, 0.28 cm^2, 15 μg_{Pt} cm^{-2}_{GC} and PtRu black electrode in O_2-saturated 0.5 mol dm^{-3} H_2SO_4 solution containing dissolved Ru species in various concentrations. The inset shows the corresponding changes to the mass-specific kinetic current densities of oxygen reduction on Pt as a function of Ru concentration of the electrolyte at three electrode potentials.

simplistic model can explain why the ORR activity diminishes progressively on Pt as a function of Ru^{n+} concentration and why the contaminated electrode behaves just as a pure Ru electrode beyond a threshold concentration[7] (see inset in Figure 6). A detailed investigation of the dynamics of Ru ad-layer formation as a function of electrode potential with and without the presence of dissolved oxygen is currently in progress.

Fundamental understanding of anion adsorption on Pt and Pt alloy electrocatalysts.
Thomas Arruda, Nagappan Ramaswamy (2nd year graduate students)

Since Halide anion adsorption on Pt was first described by Slygin in 1935, many studies have been published. Early work probing the effects of anions on hydrogen underpotential deposition (H_{upd}) on Pt suggested low concentrations of Halide anions significantly change H_{upd} peaks with respect to potential and magnitude. Other investigators have concentrated their efforts to higher potentials where oxygen reduction reaction (ORR) is expected to take place. In more recent efforts rotating ring disk experiments (RRDE) showed that even trace levels (as low as 10^{-4}M) of Cl^- significantly altered the Pt cyclic voltammagram (CV) and produced large quantities of H_2O_2.

Others have attempted to understand anion adsorption by structural elucidation of the adlayer on the surface. Surface sensitive techniques utilized include Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), and Surface X-Ray Scattering (SXS). An AES/LEED study indicated that Cl_{ads} occurred on the Pt(100) facet at lower electrode potentials than on Pt(111), suggesting that Pt(100) is more susceptible to poisoning. One common thread in the aforementioned techniques though is the necessity for an ultra high vacuum (UHV) environment. In addition, the previous studies have been performed on single crystal materials. In order to understand fuel cell relevant surface/adsorbate interactions, it is desirable to utilize *in situ* techniques on actual fuel cell catalysts. In their reports, Marković *et al*. used *in situ* SXS to probe the interaction of Pt particles with Halide anions. Surface coverage and adlayer structural information was obtained, but only on Pt(111) single crystals.

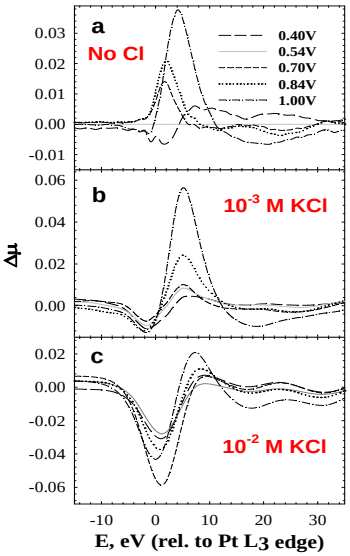

Figure 5. Pt L_3 edge $\Delta\mu = \mu(V) - \mu(0.54V$ clean) spectra as a function of electrode potential in (a) 1M $HClO_4$ (clean), (b) 1M $HClO_4$ + 1mM KCl and (c) 1M $HClO_4$ +10mM KCl. The peak

Figure 5 shows the resulting $\Delta\mu$ curves for Pt/C in clean 1M $HClO_4$, and the corresponding solutions contaminated with 1 and 10mM KCl. Figure 5a represents "water activation" as it occurs on Pt/C in 1M $HClO_4$ and agrees well with previously reported data. All of the data sets contain a sinusoidal line shape at 0.24V indicating a strong presence of adsorbed hydrogen (H_{ads}). In addition to a clear increase in $\Delta\mu$ peak intensity, there is a corresponding "shift" in peak position which has been attributed to a change in $O[H]_{ads}$ binding site from atop to n-fold as the electrode potential is increased. The $\Delta\mu$ curves in Figure 5b show a systematic increase in peak intensity however, there is a lack of peak shift as they are already situated at higher absorption energy (~5eV in respect to the edge). This suggests that any Cl_{ads} present impedes the formation of lower coordinated Pt-O[H] geometries (atop/bridged), thus forcing O[H] directly into 3-fold sites. Figure 5c features a large minima (~0eV) as well as a suppressed maxima in the $O[H]_{ads}$ region of the $\Delta\mu$ spectrum with little variation as the electrode potential is increased. Both the large negative peak, and the low intensity O[H] peak suggests a strong presence of Cl_{ads} at all potentials.

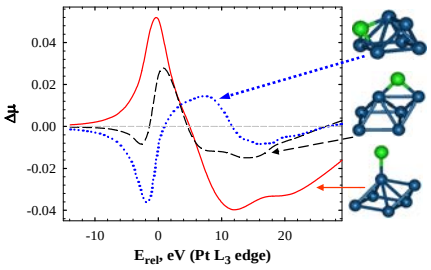

Figure 6. Theoretical $\Delta\mu$ signatures (non shifted, scaled) calculated by FEFF8.0, $\Delta\mu = \mu(Pt_6\text{-}Cl) - \mu(Pt_6)$ for (a) atop Cl, (b) bridged Cl and (c) 3-fold Cl (fcc site).

Fitting of the experimental $\Delta\mu$ curves was performed by comparison to theory calculations from FEFF8.0. Figure 6 shows the FEFF8.0 calculated $\Delta\mu$ line shapes (not shifted or scaled) with corresponding depictions of the Pt_6 cluster and adsorbed Cl with a Pt-Cl distance of 2.4Å. The solid line representing atop Pt_6-Cl contains a large maxima near the edge position followed by significant negative contribution. This line shape has not been found in the experimental data, indicating the absence of atop Pt-Cl. The dashed line representing bridged Cl resembles the line shape found in 1mM Cl^-, suggesting that at 1mM Cl^- concentration, Cl_{ads} occurs in a 2-fold configuration. This result is consistent with the lack of peak shifting found in Figure 5b. By assuming that the bridged site is occupied by Cl_{ads}, it is evident that $O[H]_{ads}$ becomes hindered until the potential is high enough for it to directly adsorb 3-fold. The FEFF calculated $\Delta\mu$ for 3-fold Cl_{ads} in Figure 6 (dotted line) compares closely with the experimental $\Delta\mu$ line shape for 10mM Cl^-, especially noting the large minima followed by a small positive peak. This result implies that Cl_{ads} occurs 3-fold at 10mM and is further supported by a lack of 3-fold O_{ads} (intense maxima in Figure 5a)

signature in the experimental Δμ spectra. The reason for a change from bridged to 3-fold with a 10 fold increase in Cl^- concentration is still unclear however.

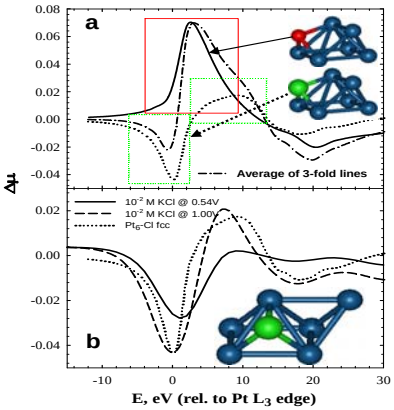

Figure 7. (a) Comparison of theoretical 3-fold O (solid) and 3-fold Cl (dotted) Δμ signatures. The dash-dot line shows the sum of the two curves. (b) Comparison of experimental Δμ

In the case of 10^{-3} M chloride the adsorption geometry is not as obvious as it was in 10^{-2} M Cl^-. The theoretical Δμ line shapes suggest bridge bonded adsorption; however, we interpret the spectra to be a combination of H_2O activation (hence presence of surface oxides) and 3-fold Cl^- adsorption occurring concurrently. There is direct evidence of both chloride and O[H] adsorption in the Δμ. To illustrate this, Figure 7a shows the FEFF 8.0 Δμ simulations for 3-fold O and 3-fold Cl^- with boxes to emphasize the major elements of each adsorbing species. Both Pt_6 clusters show 3-fold adsorption of chloride and O[H] with vastly different Δμ signatures. The dash-dot line, showing the sum of 3-fold Δμ theory exhibits an astonishing likeness to the experimental data in 10^{-3} M chloride. This is, in our opinion, the best evidence indicating 3-fold chloride adsorption occurring in parallel with 3-fold O[H] formation.

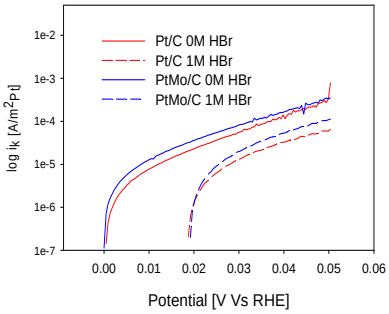

Figure 8: Tafel plots for HOR showing the activity of Pt and PtMo electrocatalysts in 0.1M $HClO_4$ electrolyte with and without 1M HBr as poison

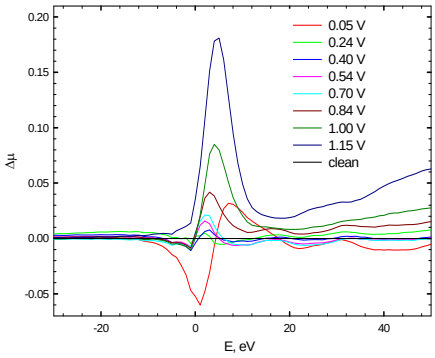

Figure 9: Experimental Δμ signatures obtained at Pt L_3 edge in deoxygenated 0.1M $HClO_4$ electrolyte with 10 mM HBr as poison

A similar effort but with technological impact is also underway in our laboratory. This involves the development of electrocatalysts H_2 oxidation/evolution (HOR/HER) in for application in H_2-Br_2 hybrid flow battery. The challenge here involves development of electrocatalyst for (HOR/HER) reaction that is also tolerant to bromide anion poisoning. Typical electrolyte used in this hybrid flow battery system is 3M HBr. Figure 8 shows the HOR activity of in house developed carbon supported PtMo in comparison to Pt/C without and without 1M HBr as the poison in deoxygenated 0.1M $HClO_4$. This indicates the superior tolerance of PtMo electrocatalyst in comparison to Pt/C. Our novel Δμ is being used in order to understand the site specific adsorption properties of bromide anions on Pt and PtMo electrocatalysts to elucidate the possible differences between Pt and PtMo as HOR electrocatalysts in the presence of bromide anions.

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